

PATENT ABSTRACTS OF JAPAN

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(54) MANUFACTURE OF ELECTROLYTE AND MANUFACTURE OF SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an electrolyte with high yield that has a long cycle life and contains small impurities by reacting an organic silane compound containing silicon and carbon with a fluorine compound in a solvent containing a nonaqueous solvent as a main constituent.

SOLUTION: An electrolyte formed from a salt of an organic fluorine and silicon compound containing silicon, fluorine and carbon elements is produced by reacting an organic silane compound containing at least silicon and carbon elements in a solvent containing a nonaqueous solvent as a main constituent. This electrolyte is placed in the battery housing of a secondary battery. Because the electrolyte hardly absorbs water content by itself, when it is used for a secondary battery, in particular a secondary battery utilizing an intercalation and a deintercalation reaction of lithium ions for charging and discharging, the water content in the electrolyte can easily be controlled with low density. Consequently, the reaction between a metal such as lithium or the like deposited by charge reaction and the water content is suppressed, so that the cycle life of the nonaqueous secondary battery can be prolonged.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the electrolytic manufacture approach of offering the long rechargeable battery of a cycle life with little performance degradation by the repeat of charge and discharge, in the rechargeable battery which used the intercalation reaction and deintercalation reaction of a rechargeable battery, especially a lithium ion for charge and discharge.

[0002]

[Description of the Prior Art] Since CO₂ capacity contained in atmospheric air is increasing recently, it is predicted that warming of the earth arises according to greenhouse effect. For this reason, it is becoming difficult to newly build the thermal power station which discharges CO₂ gas so much. Therefore, it stores in the rechargeable battery which installed the Nighttime power in ordinary homes as a deployment of the power made with generators, such as a thermal power station, and the so-called load leveling which equalizes a load at day ranges with much power consumption using this is proposed. Moreover, development of the rechargeable battery of a high energy consistency is expected from the electric vehicle which has the description of not discharging an atmospheric pollutant as an indispensable rechargeable battery. Furthermore, for the power-source application of portable devices, such as a book mold personal computer, a word processor, a video camera, and a cellular phone, development of a small, lightweight, and highly efficient rechargeable battery is pressing need.

[0003] As such a small, lightweight, and highly efficient rechargeable battery At the reaction at the time of charge, the lithium intercalation compound which deintercalates a lithium ion from between layers is used for the positive-electrode matter. The rechargeable battery which uses a metal lithium for a negative electrode, and the carbon material represented by the graphite which can intercalate a lithium ion between the layers of the six membered ring reticulated flat surface formed by the carbon atom to the negative-electrode matter Development of the so-called "lithium ion battery" of the used rocking chair mold is furthered (on this application specifications). The rechargeable battery which used the intercalation and day intercalation reaction of a lithium ion by charge and discharge below is called a lithium secondary battery including the "lithium ion battery" which uses a carbon material for a negative electrode.

[0004] However, the cycle life of charge and discharge is very short, and the lithium secondary battery of the high capacity which uses a metal lithium for a negative electrode has not resulted in practical use level. According to research of this invention persons, the cycle life of the charge and discharge of a lithium secondary battery which use a metal lithium for a negative electrode as a very short cause of main A metal lithium reacts with impurities, such as moisture in the electrolytic solution, and an organic solvent, and an insulator layer is formed. Owing to this, by the repeat of charge and discharge, a lithium metal grows in the shape of a dendrite (tree), and causes the internal short circuit between a negative electrode and a positive electrode, Or the dissociated electrolyte becoming a polymerization initiator, the organic solvent of the electrolytic solution carrying out a polymerization, the impedance inside a cell increasing, and disassembly of the electrolytic solution also being promoted by the repeat of charge and

discharge, and resulting in a life is presumed.

[0005] Moreover, when the dendrite of an above-mentioned lithium grows and a negative electrode and a positive electrode change into a short circuit condition, by generating heat, when the energy which a cell has is consumed by the short circuit for a short time, or the solvent of the electrolytic solution decomposing and generating gas, internal pressure may high-feel easy and may damage a cell.

[0006] the negative electrode which, on the other hand, consists of "lithium ion batteries" mentioned above with the carbon material of graphite structure -- theoretical -- per [1 / a maximum of] carbon atom -- since only the lithium atom of / 6 can be intercalated, the rechargeable battery of the high energy consistency which is equal to the lithium primary cell when using a metal lithium for the negative-electrode matter is not realizable. When it is going to intercalate the amount of lithiums more than the amount of theory in the carbon material negative electrode of a "lithium ion battery" at the time of charge A lithium metal deposits on a carbon material negative-electrode front face, a metal lithium reacts with impurities, such as moisture in the electrolytic solution, and an organic solvent like the case of the cell which uses an above-mentioned lithium metal for a negative electrode, and an insulator layer is formed. It grows up in the shape of a dendrite (tree) by the repeat of a charge-and-discharge cycle, the internal short circuit between a negative electrode and a positive electrode is caused, and it results in a life. In this way, cycle life sufficient in the "lithium ion battery" exceeding the geometric capacity of a graphite negative electrode to put in practical use is not acquired.

[0007] Therefore, in the lithium secondary battery, increase of energy density and reinforcement of a cycle life are desired strongly.

[0008] In order to attain this, in JP,9-82359,A, in the lithium secondary battery, the electrolyte which consists of a salt of an organic fluorine silicon compound is used, the performance degradation by the repeat of charge and discharge is reduced, and lengthening a cycle life is indicated.

[0009]

[Problem(s) to be Solved by the Invention] In the rechargeable battery which used for charge and discharge the intercalation reaction and deintercalation reaction of the electrolyte of the high performance which offers the long rechargeable battery of a cycle life, especially a lithium ion, this invention raises the performance degradation by the repeat of charge and discharge, and it aims at an impurity manufacturing the electrolyte of useful high performance by high yield few in order to improve a cycle life.

[0010]

[Means for Solving the Problem] This invention offers the method of manufacturing the electrolyte which consists of a salt of the organic fluorine silicon compound containing a silicon element, a fluorine element, and a carbon element of having the process to which the organic silane compound which contains a silicon element and a carbon element at least in the solvent which uses a non-aqueous solvent as a principal component, and a fluorine compound are made reacting.

[0011] Furthermore, this invention is the manufacture approach of a rechargeable battery of having used for charge and discharge the intercalation reaction and deintercalation reaction of the lithium ion of structure which held the positive electrode, the negative electrode, and the separator in cell housing at least. By the approach of having the process to which the organic silane compound which contains a silicon element and a carbon element at least in the solvent which uses the above-mentioned non-aqueous solvent as a principal component, and a fluorine compound are made reacting, a silicon element, The electrolyte which consists of a salt of the organic fluorine silicon compound containing a fluorine element and a carbon element is obtained, and the manufacture approach of the rechargeable battery which arranges this electrolyte in cell housing is offered.

[0012]

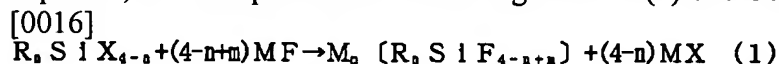
[Embodiment of the Invention] By the manufacture approach of the electrolyte of this invention, the impurity made it possible to manufacture an electrolyte few at high yield by making an organic silane compound and a fluorine compound react in the solvent which uses a non-aqueous solvent as a principal component. This is considered that it can reduce generation of an impurity, in order that the rate the fluorine ion the substituent of an organic silane compound is the reaction phase permuted by fluorine

ion, and is [ion] an anion since there are few anions, such as a hydroxide ion, in the solvent which uses a non-aqueous solvent as a principal component, a hydroxide ion, etc. carry out [a rate] competitive reaction may decrease and the substitution reaction of a fluorine element may progress preferentially. Moreover, it is thought that the interaction between fluorine ion and other ion cannot happen easily since there is little ion which exists in a solvent from the first, the above-mentioned substitution reaction occurs efficiently when free fluorine ion increases, and yield increases the solvent which uses a non-aqueous solvent as a principal component. Furthermore, when an aprotic solvent is used for the solvent which uses a non-aqueous solvent as a principal component, since most anions in a solvent can be lost, the further reduction of an impurity is attained. Moreover, if it is the non-aqueous solvent which melts an organic silane compound and a fluorine compound, since the concentration of an organic single molecule-like silane compound and fluorine ion will increase more, a substitution reaction occurs still more efficiently and increase of yield is attained.

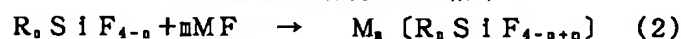
[0013] Moreover, as well as the above when using the compound which already has a fluorine element as a substituent of a silicon element as an organic silane compound, since there are few other anions, in a non-aqueous solvent, it is thought that generation of an impurity is suppressed that desorption of fluorine ion cannot happen easily.

[0014] Thus, since the electrolyte itself cannot adsorb moisture easily, when the electrolyte which consists of a salt of the organic fluorine silicon compound which contains the silicon element obtained, a fluorine element, and a carbon element at least is used as an electrolyte of the rechargeable battery which used the intercalation reaction and deintercalation reaction of a rechargeable battery, especially a lithium ion for charge and discharge, it becomes easy to manage the moisture in the electrolytic solution to low concentration. Consequently, since the reaction of metals, such as a lithium which deposits at a charge reaction, and moisture can be suppressed, the cycle life of a nonaqueous rechargeable battery can be prolonged. Moreover, a charge-and-discharge cycle life can be prolonged in the nonaqueous rechargeable battery which used this electrolyte in the above-mentioned electrolyte since the catalytic activity as an initiator of a polymerization reaction was low and the polymerization of the solvent in the electrolytic solution was suppressed.

[0015] At the process to which the organic silane compound in the manufacture approach of this invention which contains a silicon element and a carbon element at least in the solvent which uses a non-aqueous solvent as a principal component, and a fluorine compound are made to react, it is expected, for example that the following formula (1) or the reaction process of (2) advances.



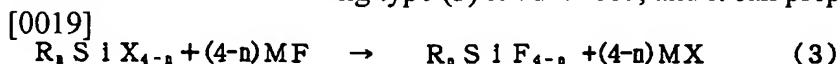
非水溶媒を主成分とする溶媒



非水溶媒を主成分とする溶媒

[0017] $R_n Si X_{4-n}$ and $R_n Si F_{4-n}$ are organic silane compounds among the above-mentioned formula, the R is an alkyl group, an aryl group, an alkenyl radical, an alkynyl group, etc., and X is a halogen halogen radical, a hydroxyl group, an alkoxy group, an acyloxy radical, an ARENOKISHI radical, an amino group, hydrogen, etc. (when there are two or more R or X, you may have a mutually different radical in the above-mentioned group, respectively). Moreover, MF is a fluorine compound and M is a metal (ion), ammonium, etc. 1-3m of n are 1 or 2.

[0018] In addition, about $R_n Si F_{4-n}$ used by (2) formulas, an organic silane compound and a fluorine compound are made to react in the solvent which uses a non-aqueous solvent as a principal component, the reaction of the following type (3) is advanced, and it can prepare.



非水溶媒を主成分とする溶媒

[0020] Thus, by the approach of this invention, an organic silane compound and a fluorine compound are set at the process to which a non-aqueous solvent is made to react in the solvent used as a principal component. The above (1) thru/or the reaction of (3) are advanced. Finally For example, a silicon element, the salt (the lithium salt expressed with a general formula $Mm [R_nSiF_{4-n+m}]$, sodium salt, potassium salt, ammonium salt, and quaternary ammonium salt -- since -- the becoming salt) of the organic fluorine silicon compound containing a fluorine element and a carbon element and the electrolyte which consists of such mixture are obtained. Since the electrolyte which consists of a salt of the organic fluorine silicon compound which contains such a silicon element, a fluorine element, and a carbon element at least can suppress the reaction of metals, such as a lithium which deposits at a charge reaction, and moisture when the electrolyte itself cannot adsorb moisture easily as mentioned above, as a result it is used as an electrolyte of a lithium secondary battery, it can prolong the cycle life of a nonaqueous rechargeable battery.

[0021] Moreover, the electrolytic solution of higher ionic conductivity can be obtained, since it is easy to dissolve the salt of an organic fluorine silicon compound with aryl groups, such as a phenyl group, in an organic solvent, with the lithium secondary battery which used especially this electrolytic solution, internal impedance can be reduced, it becomes possible to pass a bigger current and a charge-and-discharge cycle life also becomes long.

[0022] Next, the manufacture approach of the electrolyte of this invention sticks like 1 operative condition, and it explains. In the embodiment concerned, stir an organic silane compound and a fluorine compound, they are made to react fundamentally in the solvent which uses a non-aqueous solvent as a principal component, and the organic target fluorine silicon compound is compounded. The concrete example of a production process is explained to a detail with reference to drawing 1 below.

[0023] First, the air dried in the well-closed container which attached reflux equipment and stirring equipment, nitrogen dried more preferably, or inert gas, It is filled up, and the solvent which uses a fluorine compound and a non-aqueous solvent as a principal component is put in in a container, and is stirred (process A). An organic silane compound small quantity every in the solvent which adds (process B), continues stirring after that (process C), and uses a non-aqueous solvent as a principal component The organic silane compound which contains a silicon element and a carbon element at least, a fluorine compound (1), for example, the above-mentioned formula, or the reaction of (3) is advanced. Moreover, after the above-mentioned reaction extracts, condenses and dries a compost with a conventional method (process D), a purification process (process E) is performed further more preferably, and the electrolyte which consists of a salt of an organic fluorine silicon compound is obtained.

[0024] At this time, it is desirable to warm or cool a reaction container and to keep temperature constant, and, as for temperature, controlling below 100 degrees C is desirable. When using the compound which has the high thing of substitution reaction nature, such as a halogen radical and an alkoxy group, in an organic silane compound as a substituent of a silicon element, it is more desirable to cool below to a room temperature and to raise temperature in a reaction anaphase the first half of a reaction. Moreover, in case an organic silane compound is added (process B) (dropping), it is desirable to remain as it is, if an organic silane compound is a liquid, and to add a thing with means, such as small quantity [every] dropping, by melting to the solvent which uses as a principal component the non-aqueous solvent which will be used for a reaction if an organic silane compound is a solid-state or a gas, (process B').

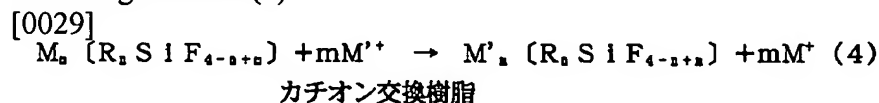
[0025] Although what is necessary is to use only the amount which is equivalent to compounding the salt of an organic fluorine silicon compound to an organic silane compound in a fluorine compound in case an organic silane compound and a fluorine compound are made to react in the solvent which uses a non-aqueous solvent as a principal component (especially process B-C), when excessive-amount use of the fluorine compound is carried out, yield is good and desirable. As a desirable amount, it is 100% - 200% more preferably 100% to 300% in a mole ratio to an organic silane compound. Moreover, although especially a limit does not have the amount of the solvent which uses a non-aqueous solvent as a principal component, when a substitution reaction uses the organic silane compound or fluorine compound which runs rapidly, it is desirable to make [many] the amount of solvents, and it is desirable to adjust so that the molality of an organic silane compound may become [kg] in one mol /or less as an

amount of solvents.

[0026] Furthermore, when a reaction condition is adjusted so that it may become three or less per silicon element about the fluorine element as a substituent of the silicon element of the salt of the compound organic fluorine silicon compound, the pyrolysis of an organic fluorine silicon compound is suppressed at the time of the concentration after a reaction, and desiccation, and it is desirable in respect of yield and an impurity.

[0027] After making an organic silane compound and a fluorine compound react, when the process which subsequently exchanges the cation of the salt of the obtained organic fluorine silicon compound for other ion kinds is performed (process F), the impurity salt from which the number of ionization of the organic fluorine silicon compound salt generated in the reaction phase of an organic silane compound and a fluorine compound differs can be reduced, and it is desirable. If the organic fluorine silicon compound salt which made the cation especially quaternary ammonium ion, such as ammonium ion and $4(C_4H_9)N^+$, in D (or E) from Process A is obtained and the cation is exchanged for alkali-metal ion, such as Li^+ , Na^+ , and K^+ , etc. at Process F, after reduction of the impurity salt from which the number of ionization differs is made efficiently, an organic fluorine silicon compound salt can be obtained. Especially, the case where it exchanges for Li^+ ion can reduce an impurity most, and is more desirable.

[0028] The exchange reaction of the ion kind in this process F advances by the reaction formula of the following formula (4).



Here, they are $M'=Li, Na, K$, etc.

[0030] After the above-mentioned ion exchange reaction extracts, condenses and dries a compost with a conventional method (process G), a purification process (process H) is performed further more preferably, and the electrolyte which consists of an organic fluorine silicon compound salt with which the ion exchange was made is obtained.

[0031] Reduction of the impurity salt from which the number of ionization differs can perform more efficiently the approach of exchanging for hydrogen by the approach, the cation exchange resin, or the film which carries out direct exchange by cation exchange resin or the film although the ion exchange means of a conventional method can use as an approach of carrying out the ion exchange, and subsequently neutralizing and exchanging by the target cation, and the approach of mixing with the salt containing the ion which makes into the purpose in a solvent, and carrying out cation exchange using ionic strength or precipitate generating, and they are desirable. [of reduction]

[0032] Next, each ingredient used is explained to a detail in the reaction of the organic silane compound in a series of processes mentioned above, and a fluorine compound.

[0033] (Solvent which uses a non-aqueous solvent as a principal component) As a solvent used by the manufacture approach of this invention, it is a non-aqueous solvent, i.e., the solvent which uses solvents other than water as a principal component, and that in which only a minute amount contains moisture is used. It is desirable that it is 95 % of the weight or more as a content of the non-aqueous solvent in a solvent, and when moisture uses the solvent which is not contained at all, generation of an impurity decreases further and is more desirable.

[0034] Moreover, when the solvent which can melt the organic silane compound containing a silicon element and a carbon element and a fluorine compound is used, an electrolyte is obtained more by high yield and is desirable. Since more compounds which contain an organic silane compound, a fluorine compound, especially a bad soluble fluorine element [as opposed to an organic solvent generally] as what has the large specific inductive capacity of a solvent is good, and specific inductive capacity is three or more (when it is the solvent temperature of 20 degrees C) can be melted as a solvent which can melt an organic silane compound and a fluorine compound, the yield of the electrolyte which is a

compost becomes high and is desirable. In addition, specific inductive capacity is a value [the dielectric constant of vacuum 1 / dielectric constant / of insulating materials such as a solvent,], and it is expressed with the following formulas.

[0035] $\epsilon = C/C_0$ (epsilon: electrostatic capacity at the time of not putting an insulating material into the electrostatic capacity at the time of putting an insulating material into specific inductive capacity and C:capacitor, and a C_0 :capacitor, but making it a vacuum)

[0036] Furthermore, when other anions which cause fluorine ion and competitive reaction use few aprotic solvents into a solvent in an electrolytic synthetic reaction phase, generation of an impurity is suppressed and it is more desirable. As an usable desirable aprotic solvent, ether, ketones, ester, amides, nitril, amines, halogenated compounds, nitro compounds, and sulfur compounds are mentioned. As a more desirable example, diethylether, diisopropyl ether, A tetrahydrofuran, tetrahydropyran, 1, 2-methoxyethane, Diethylene-glycol wood ether, an acetone, ethyl methyl ketone, A cyclohexanone, ethyl acetate, butyl acetate, ethylene carbonate, propylene carbonate, Dimethyl carbonate, a formamide, N,N-dimethylformamide, N,N-dimethylacetamide, 1,3-dimethyl-2-imidazolidinone, N-methyl pyrrolidone, an acetonitrile, propionitrile, SURISHINONI tolyl, A benzonitrile, ethylenediamine, triethyleamine, an aniline, A pyridine, a piperidine, a morpholine, a methylene chloride, chloroform, 1,2-dichloroethane, a chlorobenzene, 1-BUOMO-2-chloroethane, nitromethane, a nitrobenzene, ortho nitrotoluene, dimethyl sulfoxide, a sulfolane, etc. are mentioned. In addition, these solvents can use an independent solution or two or more sorts of mixed solutions.

[0037] (Organic silane compound) Although the silane compound which had at least one or more silicon elements, and at least one or more carbon elements have combined with this silicon element as an organic silane compound which is used by this invention, and which contains a silicon element and a carbon element at least is mentioned Since a silane compound (for example, the above-mentioned R_nSiX_{4-n}) with four substituents (the radical combined to a silicon element is called a substituent about this invention) which have one silicon element and were combined with this silicon element, and ***** are good, it is desirable in respect of the improvement in yield.

[0038] Furthermore, that in which an organic silane compound has a lifting and one to three cone substituents for fluorine ion and a substitution reaction among four substituents of a silicon element is desirable, and what already has a fluorine element as a substituent is more desirable. Fluorine ion and a substitution reaction as a lifting or a cone substituent (X of the above-mentioned formula) - Halogen radicals, such as Cl, -Br, and -I, the hydroxyl group of -OH, -OCH₃, -OC₂H₅, the alkoxy group of -OC₄H₉ grade, - Amino groups, such as an ARENOKISHI radical of the acyloxy radical of OCOCH₃ and -OCOC₂H₅ grade, -OC₆H₅, -OC₆H₄CH₃, and -OC₁₀H₇ grade, -NR₁H, and -NR one R₂ (R₁, R₂: alkyl group), and -H (hydrogen) are mentioned.

[0039] moreover, an organic silane compound -- above-mentioned fluorine ion and an above-mentioned substitution reaction -- a lifting -- being easy -- as the substituent (R of the above-mentioned formula) of the remainder in addition to a substituent -- fluorine ion and a substitution reaction -- a lifting -- being hard -- when it has a substituent, since the solubility over an organic solvent can be maintained good and a reaction advances efficiently, it is desirable during a substitution reaction. Although the substituent which a carbon element couples directly at a silicon element is mentioned to a lifting as a pile substituent R, fluorine ion and a substitution reaction - Since a reaction with fluorine ion cannot occur easily and fluorine ion is used for an effective target at a substitution reaction, the aryl group of the alkyl group of CH₃, -C₂H₅, and -C₄H₉ grade, -C₆H₅, -C₆H₄CH₃, and -C₁₀H₇ grade is desirable, and its phenyl group is more desirable in respect of solubility.

[0040] Moreover, when a substituent is the alkenyl radical and alkynyl group which have unsaturated bonds, such as a double bond and a triple bond, in a -C₂H₃, -C₄H₇, -C₂H, and -C₃H₃ grade substituent, after making a compound with this substituent react with a fluorine compound, it can be further used by performing the reaction before an addition reaction etc. about this substituent.

[0041] (Fluorine compound) As a fluorine compound used by this invention It is the compound which can generate fluorine ion (for example, the above-mentioned MF). For example, although inorganic [, such as hydrogen fluoride, fluorine gas, xenon fluoride, 4 sulfur fluoride, perchloryl fluoride and cesium

sulfate fluoride, HIPOFURUO lights, N-fluoro ammonium, and a fluoride salt,] and an organic fluorine compound can be used. In respect of handling and safety, fluoride salts, such as fluoride quarternary ammonium salt, such as a tetraethyl fluoride and a tetrabutyl fluoride, ammonium fluoride, lithium fluoride, a sodium fluoride, and a potassium fluoride, are more desirable. Especially, since an ammonium fluoride salt (quarternary ammonium salt especially shown by NH_4F and general formula R_3NF (R_3 : alkyl group)) has the especially good solubility over a non-aqueous solvent, it is desirable.

[0042] Although the above is the manufacture approach of the electrolyte of this invention, a rechargeable battery is manufactured by the usual formula using the electrolyte compounded in this way. One embodiment of the lithium secondary battery which uses hereafter the electrolyte compounded by the manufacture approach of this invention is explained with reference to drawing 3, drawing 4, and drawing 5.

[0043] Drawing 3 is the sectional view showing the outline of the configuration of a rechargeable battery. In the rechargeable battery 300 shown in this drawing, opposite arrangement and these members are held for the negative electrode 301 and the positive electrode 302 in the cell housing 307 through an electrolyte or the electrolytic solution (electrolytic solution) 303, and a separator 304. The salt of the organic fluorine silicon compound compounded by the approach of this invention is used for this electrolyte 303. It connects with a negative electrode 301 at the in-and-out force terminal 305, and a positive electrode 302 is connected to the in-and-out force terminal 306.

[0044] (Electrolytic operation) The following three kinds are mentioned as a usage within the rechargeable battery of the electrolyte (303) compounded by the approach of this invention.

- (1) How to use in the condition as it is.
- (2) How to use as a solution which dissolved in the solvent.
- (3) How to use as what was fixed by adding gelling agents, such as a polymer, in a solution.

[0045] Generally, it is used for it, making a solvent carry out liquid retaining of the electrolytic solution which melted the electrolyte to a porous separator. In addition, as for the electrolyte compounded by the manufacture approach of this invention, it is desirable to heat under reduced pressure and to perform sufficient dehydration and deoxidation.

[0046] As an electrolytic solvent, for example An acetonitrile, a benzonitrile, Propylene carbonate, ethylene carbonate, dimethyl carbonate, Diethyl carbonate, dimethylformamide, a tetrahydrofuran, A nitrobenzene, a dichloroethane, diethoxy ethane, 1, 2-dimethoxyethane, A chlorobenzene, gamma-butyrolactone, dioxolane, a sulfolane, Nitromethane, dimethyl sulfide, dimethyl ape oxide, methyl formate, 3-methyl-2-OKIDAZORIJINON, 2-methyl tetrahydrofuran, 3-propyl sydnone, sulfur dioxide, a phosphoryl chloride, a thionyl chloride, sulfuryl chlorides, or these mixed liquor can be used.

[0047] The above-mentioned solvent is good to dehydrate with an activated alumina, a molecular sieve, a phosphorus pentaoxide, a calcium chloride, etc., or to distill under alkali-metal coexistence in inert gas depending on a solvent, and to also perform impurity removal and dehydration.

[0048] Gelling is desirable in order to prevent leakage of the electrolytic solution. It is desirable to use a polymer which absorbs and swells the solvent of the electrolytic solution as a gelling agent.

Polyethylene oxide, polyvinyl alcohol, polyacrylamide, etc. are used as such a polymer. Since especially the electrolyte obtained by this invention is used for the electrolyte in a lithium secondary battery, and it can suppress the reaction of metals, such as a lithium which deposits at a charge reaction, and moisture as mentioned above, it can prolong the cycle life of a nonaqueous rechargeable battery.

[0049] Each part material at the time of using as a lithium secondary battery the rechargeable battery shown in drawing 1 is explained below.

[0050] (Positive electrode) The positive electrode (301) used for a lithium secondary battery consists of a charge collector, positive active material, an electric conduction nominal member, a binder, etc. This positive electrode fabricates positive active material, an electric conduction nominal member, and the thing that mixed whenever [binder name] on the front face of a charge collector, and is produced.

[0051] If positive active material is carried out, generally transition-metals oxide, a transition-metals sulfide, lithium transition-metals oxide, or a lithium transition-metals sulfide is used. As a transition-metals element of a transition-metals oxide or a transition-metals sulfide For example, the place which is

the element which has d husks or f husks partially, Sc and Y, Lanthanoids, actinoid one, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, nickel, Pd, Pt, Cu, Ag, and Au are mentioned. Especially, Ti which is the first sere metal, V, Cr, Mn, Fe, Co, nickel, and Cu are used suitably.

[0052] As an electric conduction adjuvant used for a positive electrode, metal impalpable powder called carbon black, such as a graphite, KETCHIEN black, and acetylene black, such as amorphous carbon and nickel, is mentioned. As a binder used for a positive electrode, fluororesin ** like polyolefines, such as polyethylene and polypropylene, or Pori fluoride kinky thread NIDEN and a tetrafluoroethylene polymer is mentioned.

[0053] Or the charge collector of a positive electrode supplies efficiently the current consumed by the electrode reaction at the time of charge, it is bearing the duty which collects the current generated at the time of discharge. Therefore, the quality of the material with it is desirable. [high and electric conductivity and] [inactive to a cell reaction as an ingredient which forms the charge collector of a positive electrode] As the desirable quality of the material, nickel, stainless steel, titanium, aluminum, copper, platinum, palladium, gold, zinc, various alloys, and the two or more above-mentioned sorts of compound metals are mentioned. As a configuration of a charge collector, configurations, such as the shape of the shape of the shape of tabular and a foil and a mesh and sponge, fibrous, a punching metal, and an expanded metal, are employable, for example. (Negative electrode) In the negative electrode (302) used for a lithium secondary battery, transition-metals oxide ** which has the ingredient which has the metallic element which forms carbon material also including graphite, a lithium metal, a lithium alloy, and a lithium and an alloy, a porosity metal, positive active material, and electromotive force is used as a negative-electrode active material used as the host material of a lithium ion. When the configuration of the above-mentioned negative-electrode active material is powder, it is made to sinter using a binder, a negative-electrode active material layer is formed on a charge collector, and a negative electrode is produced. Moreover, when the conductivity of the above-mentioned negative-electrode active material powder is low, it is necessary suitably like formation of the active material layer of a positive electrode to mix an electric conduction nominal member. As the above-mentioned charge collector and an electric conduction nominal member, what is used for said positive electrode can use it similarly.

[0054] (Separator) A separator (304) has the role which prevents the short circuit of a negative electrode and a positive electrode. Moreover, it may have a role holding the electrolytic solution (303).

[0055] A separator needs to have the pore which a lithium ion can move, and needs to be insoluble to the electrolytic solution, and needs to be stable. Therefore, as a separator, the ingredient of nonwoven fabrics, such as polyolefines, such as glass, polypropylene, and polyethylene, and a fluororesin, or micropore structure is used suitably, for example. Moreover, the metallic-oxide film which has micropore, or the resin film which compound-ized the metallic oxide can also be used. Since it is hard to penetrate a dendrite when the metallic-oxide film which has the structure multilayered especially is used, effectiveness is in short circuit prevention. When the fluororesin film which is a fire retarding material, the glass which is an incombustible material, or a metallic-oxide film is used, safety can be raised more.

[0056] (The configuration and structure of a cell) As a configuration of a rechargeable battery, there is specifically flat form, cylindrical shape, rectangular parallelepiped form, and sheet type ** etc. by making into basic structure structure shown in drawing 3 . Moreover, as structure of the member in a cell, there are a monolayer type, a multilayer type, a spiral type, etc., for example. Also in it, by winding on both sides of a separator between a negative electrode and a positive electrode, the cell of a spiral type cylindrical shape can enlarge an electrode surface product, and has the description that a high current can be passed at the time of charge and discharge. Moreover, the cell of a rectangular parallelepiped form or a sheet form has the description which can use effectively the storage space of the device which contains a cell.

[0057] Below, with reference to drawing 4 and drawing 5 , more detailed explanation is given about the configuration and structure of a cell. Drawing 4 is the sectional view of a monolayer type flat form (coin form) cell, and drawing 5 expresses the sectional view of a spiral type cylindrical shape cell. These

lithium cells are the same configurations as drawing 3 fundamentally, and it consists of a negative electrode, a positive electrode, an electrolyte and a separator, cell housing, an output terminal, etc. [0058] drawing 4 and drawing 5 -- setting -- 400 and 500 -- a negative-electrode charge collector, the separator with which a negative-electrode terminal (negative-electrode cap), and 406 and 506 held the positive-electrode can, and, as for 407 and 507, 401 and 501 held [a negative-electrode active material, and 403 and 503] the electrolytic solution as for positive active material, and 405 and 505, and 410 and 510 -- insulating packing and 511 -- an electric insulating plate -- it comes out. In the lithium secondary battery of the flat structure shown in drawing 4 The positive electrode containing positive active material 403 and the negative electrode containing the negative-electrode active material 401 and the negative-electrode charge collector 400 The layered product by which the laminating was carried out through the separator 407 holding the electrolyte which consists of a salt of the organic fluorine silicon compound which contains at least the silicon element compounded as mentioned above, a fluorine element, and a carbon element at least is held in the positive-electrode can 406 from a positive-electrode side. The negative-electrode side is covered with the negative-electrode terminal (negative-electrode cap) 405. And as for other parts in a positive-electrode can, the insulating material is arranged (insulating packing 410).

[0059] In the lithium secondary battery of the shape of a cylinder shown in drawing 5 , the positive electrode containing positive active material 503, and the negative-electrode active material 501 between negative electrodes The separator 507 holding the electrolyte which consists of a salt of the organic fluorine silicon compound which contains at least the silicon element compounded as mentioned above, a fluorine element, and a carbon element is fastened at least. The layered product of the cylindrical structure wound around multiplex centering on the predetermined shaft is held in the positive-electrode can 506 from the side-face and 1 base side. Moreover, the base (top face) side of everything but this layered product is covered with the negative-electrode terminal (negative-electrode cap) 505. And as for other parts in a positive-electrode can, the insulator is arranged (insulating packing 510). Below, an example of an approach to assemble the cell shown in drawing 4 or drawing 5 is explained.

(1) Between a negative-electrode active material layer (401 501) and the fabricated positive-active-material layer (403 503), insert a separator (407 507) and include in a positive-electrode can (406 506).

(2) Assemble a negative-electrode cap (405 505) and insulating packing (410 510) after pouring in an electrolyte.

(3) Above (2) A cell is completed by caulking *****.

[0060] In addition, as for ingredient preparation of the lithium cell mentioned above and the assembly of a cell, it is desirable to carry out in the dry air from which moisture was removed enough, or desiccation inert gas.

[0061] (Insulating packing) As an ingredient of a gasket (410 510), a fluororesin, polyamide resin, polysulfone resin, and various rubber can be used, for example. As the obturation approach of a cell, approaches, such as the glass sealed tube, adhesives, welding, and soldering, are used like drawing 4 and drawing 5 besides the "caulking" using insulating packing.

[0062] Moreover, various organic resin ingredients and the ceramics are used as an ingredient of the electric insulating plate of drawing 5 .

[0063] (Outside can) The can is constituted by the positive-electrode can (406 506) of a cell, and the negative-electrode cap (405,505) outside the cell. As an ingredient of an outside can, stainless steel is used suitably. Especially, a titanium clad stainless plate, a copper clad stainless plate, a nickel-plating steel plate, etc. are used abundantly.

[0064] In the mode shown in drawing 4 and drawing 5 , since the positive-electrode can (406 506) serves as cell housing, the above-mentioned stainless steel is desirable. However, when a positive-electrode can does not make cell housing serve a double purpose, as the quality of the material of cell housing, the composite of plastics, such as metals, such as zinc, and polypropylene, a metal or a glass fiber, and plastics is used besides stainless steel.

[0065] (Relief valve) The lithium secondary battery is equipped with the relief valve as a safety practice

when the internal pressure of a cell increases. Although not illustrated by drawing 4 and drawing 5, as a relief valve, rubber, a spring, a metal ball, a burst foil, etc. can be used, for example.

[0066] Hereafter, this invention is explained to a detail based on an example. This invention is not limited to these examples. In addition, there are weight criteria among a sentence with the section and %.

[0067] an example 1 (composition of an organic fluorine silicon compound salt) -- it was filled up with the nitrogen gas first dried in the reaction container of the three-neck flask which attached reflux equipment, stirring equipment, and a dropping funnel. In this three-neck flask, the diethylether (99.5% of purity) 100 section dried by the tetra-n-butyl ammonium FUROORIDO (n-Bu) 4NF(99% of purity) 10.4 section (0.04 mols) and molecular-sieve 3A which carried out the vacuum drying at 50 degrees C, and removed moisture was put in, and it stirred until it could solve tetra-n-butyl ammonium FUROORIDO. In addition, when the moisture content of diethylether after drying by the molecular sieve was measured with the curl Fischer moisture meter, it was 0.5%, and when the specific inductive capacity of diethylether after drying by the molecular sieve was measured by Impedance Analyzer (H.P. shrine make), it was 4.3 (20 degrees C).

[0068] Next, the triphenyl chlorosilane Ph_3SiCl 15.5 section (0.02 mols) which carried out the vacuum drying at 50 degrees C, and removed moisture was melted in the diethylether 100 same dry section as the above, and this solution was put in in the dropping funnel of the above-mentioned reaction container.

[0069] The above-mentioned reaction container was cooled at 0 degree C by the ice bath, and while the solution in a dropping funnel was dropped gradually, stirring the inside of a container, it added in the container. It stirred at 0 degree C after addition for 1 hour, subsequently to 50 degrees C it warmed, and stirring was continued for further 2 hours.

[0070] Cold water washed the crystal which condensed diethylether of a solvent by the rotary evaporator after reaction termination, dried and was obtained after that, the tetra-n-butyl ammonium chloride which is a by-product was removed, and 4Ns (n-Bu) $[\text{Ph}_3\text{SiF}_2]$ of the target triphenyl difluoro silicic acid tetra-n-butyl ammonium salt were obtained.

[0071] (Ion exchange of an organic fluorine silicon compound salt) The triphenyl difluoro silicic acid tetra-n-butyl ammonium salt and the tetrafluoroboric lithium LiBF_4 (98% of purity) which were obtained above were melted to the acetone, and it condensed by the rotary evaporator after 2-hour stirring, and cold water washed the crystal which dried and was obtained after that, the tetrafluoroboric tetra-n-butyl ammonium salt which is a by-product was removed, and target triphenyl difluoro silicic acid lithium salt $\text{Li} [\text{Ph}_3\text{SiF}_2]$ was obtained.

[0072] Except using the mixed water solution of diethylether/water (10% : 90%) for a change of desiccation diethylether used in the example of comparison 1 (composition of an organic fluorine silicon compound salt) example 1, the same processing as an example 1 was performed, and 4Ns (n-Bu) $[\text{Ph}_3\text{SiF}_2]$ of triphenyl difluoro silicic acid tetra-n-butyl ammonium salt were obtained.

[0073] It was first filled up with the nitrogen gas dried in the reaction container of the three-neck flask which attached reflux equipment, stirring equipment, and a dropping funnel like example 2 (composition of an organic fluorine silicon compound salt) example 1. In this three-neck flask, the dimethylsulfoxide (99% of purity) 80 section dried by the tetraethylammonium FUROORIDO Et_4NF (99% of purity) 9.0 section (0.06 mols) and molecular-sieve 3A which carried out the vacuum drying at 50 degrees C, and removed moisture was put in, and it stirred until it could solve tetraethylammonium FUROORIDO. In addition, when the moisture content of dimethylsulfoxide after drying by the molecular sieve was measured with the curl Fischer moisture meter, it was 0.05%, and when the specific inductive capacity of dimethylsulfoxide after drying by the molecular sieve was measured by Impedance Analyzer, it was 48.9 (20 degrees C).

[0074] Next, the diphenyl dichlorosilane Ph_2SiCl_2 25.1 section (0.02 mols) which carried out the vacuum drying at 50 degrees C, and removed moisture was melted in the dimethylsulfoxide 80 same dry section as the above, and this solution was put in in the dropping funnel of the above-mentioned reaction container.

[0075] With the same approach as an example 1, it is the target diphenyl trifluoro silicic acid tetraethylammonium salt below. Et₄N [Ph₂SiF₃] was obtained.

[0076] (Ion exchange of an organic fluorine silicon compound salt) The diphenyl trifluoro silicic acid tetraethylammonium salt and lithium perchlorate LiClO₄ (98% of purity) which were obtained above were melted to the acetone, and it condensed by the rotary evaporator after 2-hour stirring, and cold water washed the crystal which dried and was obtained after that, the perchloric acid tetraethylammonium salt which is a by-product was removed, and target diphenyl trifluoro silicic acid lithium salt Li [Ph₂SiF₃] was obtained.

[0077] Except using the mixed water solution of dimethyl sulfoxide/water (30% : 70%) for a change of the desiccation dimethyl sulfoxide used in the example of comparison 2 (composition of an organic fluorine silicon compound salt) example 2, the same processing as an example 2 is performed, and it is a diphenyl trifluoro silicic acid tetraethylammonium salt. Et₄N [Ph₂SiF₃] was obtained.

[0078] It was first filled up with the nitrogen gas dried in the reaction container of the three-neck flask which attached reflux equipment, stirring equipment, and a dropping funnel like example 3 (composition of an organic fluorine silicon compound salt) example 1. In this three-neck flask, the acetonitrile (99.5% of purity) 100 section dried by the ammonium fluoride NH₄F (97% of purity) 3.7 section (0.1 mols) and molecular-sieve 3A which carried out the vacuum drying at 50 degrees C, and removed moisture was put in, and it stirred until it could undo ammonium fluoride. In addition, when the moisture content of the acetonitrile after drying by molecular-sieve 3A was measured with the curl Fischer moisture meter, it was 0.1%, and when the specific inductive capacity of the acetonitrile after drying by the molecular sieve was measured by Impedance Analyzer, it was 37.5 (20 degrees C).

[0079] The phenylmethyldimethoxysilane PhMeSi(OMe)₂ 3.6 section (0.02 mols) which carried out the vacuum drying at 50 degrees C, and removed moisture next was melted in the acetonitrile 80 same dry section as the above, and this solution was put in in the dropping funnel of the above-mentioned reaction container.

[0080] By the same approach as an example 1, the target phenylmethyl trifluoro silicic acid ammonium salt NH₄ [PhMeSiF₃] was obtained below.

[0081] (Ion exchange of an organic fluorine silicon compound salt) The phenylmethyl trifluoro silicic acid ammonium salt and the hexafluoro phosphoric acid lithium LiPF₆ (99% of purity) which were obtained above were melted to the acetonitrile, and it condensed by the rotary evaporator after 2-hour stirring, and cold water washed the crystal which dried and was obtained after that, the hexafluoro ammonium phosphate salt which is a by-product was removed, and target phenylmethyl trifluoro silicic acid lithium salt Li [PhMeSiF₃] was obtained.

[0082] Except using the mixed water solution of an acetonitrile/water (50% : 50%) for a change of the desiccation acetonitrile used in the example of comparison 3 (composition of an organic fluorine silicon compound salt) example 3, the same processing as an example 3 was performed, and the phenylmethyl trifluoro silicic acid ammonium salt NH₄ [PhMeSiF₃] was obtained.

[0083] It was first filled up with the nitrogen gas dried in the reaction container of the three-neck flask which attached reflux equipment, stirring equipment, and a dropping funnel like example 4 (composition of an organic fluorine silicon compound salt) example 1. In this three-neck flask, the chlorobenzene (99.5% of purity) 120 section dried by the ammonium fluoride NH₄F (97% of purity) 3.7 section (0.1 mols) and the molecular sieve which carried out the vacuum drying at 50 degrees C, and removed moisture was put in, and it stirred until it could undo ammonium fluoride. In addition, when the moisture content of the chlorobenzene after drying by molecular-sieve 3A was measured with the curl Fischer moisture meter, it was 0.005%, and when the specific inductive capacity of the chlorobenzene after drying by the molecular sieve was measured by Impedance Analyzer, it was 5.6 (20 degrees C).

[0084] The phenyltriethoxysilane PhSi(OEt)₃ 4.8 section (0.02 mols) which carried out the vacuum drying at 50 degrees C, and removed moisture next was melted in the chlorobenzene 50 same dry section as the above, and this solution was put in in the dropping funnel of the above-mentioned reaction container.

[0085] By the same approach as an example 1, the target phenyl pentafluoro silicic acid ammonium salt

(NH₄) [PhSiF₅] 2 was obtained below.

[0086] (Ion exchange of an organic fluorine silicon compound salt) The phenyl pentafluoro silicic acid ammonium salt obtained above was melted to the acetonitrile, it let the acetonitrile solution pass in the column filled up with cation-exchange-resin diamond ion SK1B, subsequently to this solution the lithium hydroxide (99% of purity) was added, and it stirred for 2 hours. This solution was condensed by the rotary evaporator after that, it dried and target phenyl pentafluoro silicic acid lithium salt Li₂ [PhSiF₅] was obtained.

[0087] Except using water for a change of the desiccation chlorobenzene used in the example of comparison 4 (composition of an organic fluorine silicon compound salt) example 4, the same processing as an example 4 was performed, and the phenyl pentafluoro silicic acid ammonium salt (NH₄) [PhSiF₅] 2 was obtained.

[0088] It was first filled up with the nitrogen gas dried in the reaction container of the three-neck flask which attached reflux equipment, stirring equipment, and a dropping funnel like example 5 (composition of an organic fluorine silicon compound salt) example 1. The lithium fluoride (98% of purity) 2.6 section (0.1 mols) and the ethyl-methyl-ketone (99.5% of purity) 200 section made to absorb moisture which carried out the vacuum drying at 50 degrees C, and removed moisture in this three-neck flask were put in and stirred. In addition, when the moisture content of this ethyl methyl ketone was measured with the curl Fischer moisture meter, it was 3.5%, and when the specific inductive capacity of this ethyl methyl ketone was measured by Impedance Analyzer, it was 18.9 (20 degrees C).

[0089] Next, ethyl triacetoxysilane EtSi(OCOCH₃)₃ 3 dried at 50 degrees C It remained as it is and the 4.7 sections (0.02 mols) were put in in the dropping funnel of the above-mentioned reaction container.

[0090] By the same approach as an example 1, target ethyl pentafluoro silicic acid lithium salt Li₂ [EtSiF₅] was obtained below (in addition, the process of the ion exchange is not performed).

[0091] Except using water for a change of the ethyl methyl ketone used in the example of comparison 5 (composition of an organic fluorine silicon compound salt) example 5, the same processing as an example 5 was performed, and ethyl pentafluoro silicic acid lithium salt Li₂ [EtSiF₅] was obtained.

[0092] It was first filled up with the nitrogen gas dried in the reaction container of the three-neck flask which attached reflux equipment, churning equipment, and a dropping funnel like example 6 (composition of an organic fluorine silicon compound salt) example 1. In this three-neck flask, the diethylether (99.5% of purity) 100 section dried by the tetraethylammonium FUROORIDO Et₄NF(99% of purity) 15.0 section (0.10 mols) and molecular-sieve 3A which carried out the vacuum drying at 50 degrees C, and removed moisture was put in, and it agitated until it could solve tetraethylammonium FUROORIDO. In addition, it is Impedance about the specific inductive capacity of diethylether when the moisture content of diethylether after drying by the molecular sieve is measured with a curl Fischer moisture meter, after being 0.5% and drying by the molecular sieve. When measured by Analyzer, it was 4.3 (20 degrees C).

[0093] Next, the vinyltriethoxysilane CH₂=CHSi(OC₂H₅)₃ 33.8 section (0.02 mols) which carried out the vacuum drying at 50 degrees C, and removed moisture was melted in the diethylether 100 same dry section as the above, and this solution was put in in the dropping funnel of the above-mentioned reaction container.

[0094] By the same approach as an example 1, the target vinyl pentafluoro silicic acid tetraethylammonium salt (Et₄N) [CH₂=CHSiF₅] 2 was obtained below.

[0095] (Ion exchange of an organic fluorine silicon compound salt) The vinyl pentafluoro silicic acid tetraethylammonium salt and lithium perchlorate LiClO₄ (98% of purity) which were obtained above were melted to the acetone, and it condensed by the rotary evaporator after 2-hour churning, and cold water washed the crystal which dried and was obtained after that, the perchloric acid tetraethylammonium salt which is a by-product was removed, and target vinyl pentafluoro silicic acid lithium salt Li₂ [CH₂=CHSiF₅] was obtained.

[0096] Except using the mixed water solution of diethylether/water (30% : 70%) for a change of desiccation diethylether used in the example of comparison 6 (composition of an organic fluorine silicon compound salt) example 6, the same processing as an example 6 was performed, and vinyl pentafluoro

silicic acid lithium salt $\text{Li}_2[\text{CH}_2=\text{CHSiF}_5]$ was obtained.

[0097] (The evaluation approach) It was estimated that yield and the amount of impurities were measured, respectively, the case of an example and the example of a comparison was compared, respectively like the example 1, the example 1 of a comparison and an example 2, and the example 2 of a comparison, and yield, the amount of impurities, and the amount of impurities after the ion exchange were indicated below about the compound of the organic fluorine silicon obtained in examples 1-6 and the examples 1-6 of a comparison.

[0098] Consequently, altogether, as indicated to Table 1, the organic fluorine silicon compound salt obtained in the example had good yield to each example of a comparison, and there were also few rates of an impurity.

[0099]

[Table 1]

表 1

	反応に使用した材料		反応生成物	収量* ¹	不純物量* ²	イオン交換後の生成物	イオン交換後の不純物量* ³
実施例 1	非水溶媒	ジエチルエーテル	$(n\text{-Bu})_4\text{N}[\text{Ph}_3\text{SiF}_4]$	4.9	0.1	$\text{Li}[\text{Ph}_3\text{SiF}_4]$	0.06
	有機シラン化合物	Ph_3SiCl					
	フッ素化合物	$(n\text{-Bu})_4\text{NF}$					
実施例 2	非水溶媒	ジメチルスルホキシド	$\text{Et}_4\text{N}[\text{Ph}_3\text{SiF}_4]$	6.1	0.05	$\text{Li}[\text{Ph}_3\text{SiF}_4]$	0.04
	有機シラン化合物	Ph_3SiCl_2					
	フッ素化合物	Et_4NF					
実施例 3	非水溶媒	アセトニトリル	$\text{NH}_4[\text{PhMeSiF}_4]$	4.7	0.1	$\text{Li}[\text{PhMeSiF}_4]$	0.07
	有機シラン化合物	$\text{PhMeSi}(\text{OMe})_2$					
	フッ素化合物	NH_4F					
実施例 4	非水溶媒	クロロベンゼン	$(\text{NH}_4)_2[\text{PhSiF}_6]$	4.2	0.2	$\text{Li}_2[\text{PhSiF}_6]$	0.09
	有機シラン化合物	$\text{PhSi}(\text{OEt})_3$					
	フッ素化合物	NH_4F					
実施例 5	非水溶媒	エチルメチルケトン	$\text{Li}_2[\text{EtSiF}_6]$	2.4	0.2	—	—
	有機シラン化合物	$\text{EtSi}(\text{OCOCH}_3)_2$					
	フッ素化合物	LiF					
実施例 6	非水溶媒	ジエチルエーテル	$(\text{Et}_4\text{N})_2[\text{CH}_2=\text{CHSiF}_4]$	2.3	0.3	$\text{Li}_2[\text{CH}_2=\text{CHSiF}_4]$	0.09
	有機シラン化合物	$\text{CH}_2=\text{CHSi}(\text{OEt})_3$					
	フッ素化合物	Et_4NF					

*1 About the weight of the salt of the organic fluorine silicon compound obtained in the yield example, it is an example of a comparison like the following formulas. It compared and judged.

Yield = weight *2 of the organic fluorine silicon compound salt obtained in the weight / example of a comparison of the organic fluorine silicon compound salt obtained in the example The amount of impurities, * 3 The salt of the impure amount-of-resources profit **** organic fluorine silicon compound after the ion exchange, and the salt of the organic fluorine silicon compound after the ion exchange The high speed liquid chromatography was used, yield was measured by having used p-toluenesulfonic-acid tetra-n-butyl ammonium salt as the internal standard reagent, and it judged compared with the example of a comparison like the following formulas.

Amount of impurities = (1- measurement concentration of organic fluorine silicon compound salt obtained in example) (measurement concentration of /internal standard reagent)/(1- measurement concentration of the organic fluorine silicon compound salt obtained in the example of a comparison) (measurement concentration of a /internal standard reagent)

Amount of impurities = (1- measurement concentration of organic fluorine silicon compound salt after the ion exchange acquired in example) (measurement concentration of /internal standard reagent)/after the ion exchange (1- measurement concentration of the organic fluorine silicon compound salt obtained in the example of a comparison) (measurement concentration of a /internal standard reagent)

Measurement concentration: Each area % to the grand total of area % of all the components in high-performance-chromatography measurement [0100] Moreover, the lithium salt of the organic fluorine silicon compound obtained in the examples 1-6 was used, the coin mold rechargeable battery indicated to drawing 4 was produced, and charge and discharge were performed. Below, the production procedure of each structure of a cell and the assembly of a cell are explained.

[0101] The lithium salt of the organic fluorine silicon compound obtained in the production examples 1-6 of the electrolytic solution was melted to the propylene carbonate solvent, respectively, and the electrolytic solution of 1M (mol/l) was produced.

[0102] After mixing the production lithium carbonate and cobalt carbonate of a positive electrode 403 by the mole ratio of 1:2, it heat-treated by 800-degree-C airstream, and the lithium-cobalt oxide was adjusted. 92% of this lithium-cobalt oxide, 3% of acetylene black carbon powder, and 5% of polyvinylidene fluoride powder were added to the N-methyl-2-pyrrolidone, the paste was adjusted, after carrying out spreading desiccation, reduced pressure drying was carried out to the charge collector which is expanded metal-like aluminium foil at 150 degrees C, and the positive electrode 403 was produced.

[0103] It added to 95% of impalpable powder of the natural graphite heat-treated at 2000 degrees C among the production argon gas air current of a negative electrode 402, and 5% N-methyl-2-pyrrolidone of polyvinylidene fluoride powder, and the paste was adjusted, after carrying out spreading desiccation, reduced pressure drying was carried out to the charge collector which is copper foil at 150 degrees C, and the negative electrode 402 was produced.

[0104] the fine hole of separator polyethylene -- the separator was used.

[0105] In the assembly argon gas ambient atmosphere of a cell, the separator 407 to which liquid retaining of the electrolytic solution was carried out was inserted between the negative electrode 402 and the positive electrode 403, and it inserted in the positive-electrode can 406 of the stainless steel material of a titanium clad. The insulating packing 410 of polypropylene and the negative-electrode cap 405 of the stainless steel material of a titanium clad were put on the obtained positive-electrode can 406, and the ***** lithium secondary battery was obtained.

[0106] Drawing 2 is a 0.4mA o'clock [of discharge currents of the rechargeable battery which used the lithium salt of the organic fluorine silicon compound of an example 1] discharge curve, and good charge/discharge capability ability was obtained. In addition, the lithium salt of the organic fluorine silicon compound obtained in other examples was also the same good charge/discharge capability ability as an example 1.

[0107]

[Effect of the Invention] As explained above, according to the manufacture approach of the electrolyte of this invention, it enables an impurity to manufacture the electrolyte which offers the long lithium secondary battery of a cycle life with little performance degradation by the repeat of charge and discharge by high yield few.

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the electrolyte which consists of a salt of the organic fluorine silicon compound containing a silicon element, a fluorine element, and a carbon element characterized by having the process to which the organic silane compound which contains a silicon element and a carbon element at least, and a fluorine compound are made to react in the solvent which uses a non-aqueous solvent as a principal component.

[Claim 2] The manufacture approach of the electrolyte according to claim 1 which is an electrolyte with which said electrolyte uses the intercalation reaction and deintercalation reaction of a lithium ion for the rechargeable battery used for charge and discharge.

[Claim 3] The manufacture approach of the electrolyte according to claim 1 or 2 which compounds the salt of an organic fluorine silicon compound at the process to which said organic silane compound and fluorine compound are made to react.

[Claim 4] The manufacture approach of an electrolyte according to claim 1 to 3 that the solvent which uses said non-aqueous solvent as a principal component is a solvent which contains a non-aqueous solvent 95% of the weight or more.

[Claim 5] The manufacture approach of an electrolyte according to claim 1 to 4 that the solvent which uses said non-aqueous solvent as a principal component is a solvent which can melt said organic silane compound and said fluorine compound.

[Claim 6] The manufacture approach of an electrolyte according to claim 5 that the solvents which use said non-aqueous solvent as a principal component are three or more specific inductive capacity when the temperature of a solvent is 20 degrees C.

[Claim 7] The manufacture approach of an electrolyte according to claim 1 to 6 that said non-aqueous solvent is an organic solvent.

[Claim 8] The manufacture approach of the electrolyte according to claim 6 which is an aprotic solvent more than a kind at least that said non-aqueous solvent is chosen from ether, ketones, ester, amides, nitril, amines, halogenated compounds, nitro compounds, and sulfur compounds.

[Claim 9] The manufacture approach of an electrolyte according to claim 1 that said fluorine compound is a fluoride salt.

[Claim 10] The manufacture approach of an electrolyte according to claim 9 that said fluoride salt is an ammonium fluoride salt.

[Claim 11] The manufacture approach of the electrolyte according to claim 10 which said organic silane compound and said ammonium fluoride salt are made to react, and compounds the ammonium salt of an organic fluorine silicon compound.

[Claim 12] The manufacture approach of the electrolyte according to claim 3 characterized by performing the process which uses the salt of said compound organic fluorine silicon compound as an intermediate product, and subsequently carries out the ion exchange of the cation and alkali-metal cation of this salt.

[Claim 13] The manufacture approach of an electrolyte according to claim 12 that said alkali-metal

cation is a lithium ion.

- [Claim 14] the process which said process which carries out the ion exchange exchanges for a hydrogen ion by the process, the cation exchange resin, or the film which carries out the direct ion exchange by cation exchange resin or the film, and subsequently neutralizes and exchanges by the target cation, and the process which mix in the salt and the solvent containing the ion made into the purpose, and carry out cation exchange using ionic strength or precipitate generating -- since -- the manufacture approach of the electrolyte according to claim 12 or 13 which is a process more than a kind chosen.

[Claim 15] The manufacture approach of the electrolyte according to claim 1 which is a compound with the substituent which said organic silane compound has from 1 a halogen radical, a hydroxyl group, an alkoxy group, an acyloxy radical, an ARENOKISHI radical, an amino group, and three substituents chosen from hydrogen as four substituents of a silicon element, and is chosen from an alkyl group and an aryl group as a remaining substituent.

[Claim 16] The manufacture approach of the electrolyte according to claim 15 which is the organic silane compound in which said organic silane compound has at least one or more phenyl groups as a substituent of a silicon element.

[Claim 17] The manufacture approach of the electrolyte according to claim 1 made into the conditions which adjust the fluorine element as a substituent of the silicon element of the salt of an organic fluorine silicon compound to three or less pieces in the process to which said organic silane compound and fluorine compound are made to react.

[Claim 18] The manufacture approach of a rechargeable battery of having the process which arranges the electrolyte which is the manufacture approach of a rechargeable battery of having used for charge and discharge the intercalation reaction and deintercalation reaction of the lithium ion of structure which held the positive electrode, the negative electrode, and the separator in cell housing at least, and was obtained by claim 1 thru/or any paddle of 17 by the approach of a publication in cell housing.

[Translation done.]